

Factors Affecting Water Quality and Surface Sediment at the Port of Tanjung Emas Semarang during the East Asian Monsoon

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Abstract: Port plays an important role in provisioning commodity needs for the society in a region. Port of Tanjung Emas Semarang (PTES) is the major port on the north coast of Java Island and serves as a port for liquid and solid goods, passengers, and fuel. This descriptive research applied a random sampling technique whose samples were taken from the port basin and control station. The research was carried out at ten stations at both high and low tides during the East Asian Monsoon. This research was aimed: a) to test the correlation of physical-chemical parameters at both high and low tide using Pearson correlation, b) to test the correlation of heavy metals (Pb, Cd, Cu, Zn) in seawater and sediment at both high and low tide, c) to perform cluster analysis on the stations at both high and low tide, d) to determine port waters Index of Pollution (IP), e) to identify factors that affect the port water pollution using PCA (Principal Component Analysis). The findings showed that in waters, Pb was found as the most dominant pollutant at both high and low tides (Pb>Cd>Cu>Zn). In sediment, Zn was the most dominant of all (Zn>Cu>Pb>Cd). I_{geo} value indicated that the contamination level in the sediment was moderate. Heavy metals accumulate differently at high and low tides, at low tide heavy metals accumulate on the outside toward the port, while at high tide they accumulate at the mouth of the Kali Baru River. This is caused by differences in the flow of tidal or ebb currents. All research stations were classified as having heavy pollution. Both control stations (Siangker and BKT estuaries) showed differences with stations inside the port, including physico-chemical variables, namely: a) TSS, phosphate, nitrate during high tide conditions; b) pH, DO, TDS, turbidity, TSS at low tide.

Keywords: control stations, Port of Tanjung Emas Semarang, East Asian Monsoon, seawater and sediment, index of pollution, principal component analysis.

东亚季风期间丹绒埃玛斯三宝垄港水质和地表泥沙的影响因素

摘要: 港口在满足一个地区社会的商品需求方面发挥着重要作用。丹绒艾玛斯三宝垄(聚四氟乙烯)港是爪哇岛北海岸的主要港口,是液体和固体货物、乘客和燃料的港口。该描述性研究采用随机抽样技术,其样本取自港口盆地和控制站。这项研究是在东亚季风期间在涨潮和退潮时的十个站点进行的。本研究旨在:一个)使用皮尔逊相关性检验涨潮和退潮时物理化学参数的相关性,b)检验海水和沉积物中重金属(Pb、Cd、Cu、Zn)在涨潮和退潮时的相关性高潮和低潮,c)对高潮和低潮站点进行聚类分析,d)确定港口水域污染指数(知识产权),电子)使用主成分分析(主成分)识别影响港口水污染的因素分析)。研究结果表明,在水域中,铅在涨潮和退潮时都是最主要的污染物(铅>镉>铜>锌)。在沉积物中,锌是最主要的(锌>铜>铅>镉)。并尾值表明沉积物中的污染水平为中等。重金属在涨潮和退潮时的积累情况不同,退潮时重金属在朝向港口的外侧积累,而在涨潮时则在卡利巴鲁的河

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口积累。这是由潮汐流或退潮流的差异引起的。所有研究站都被列为重度污染。两个控制站（香客和 BKT 河口）都显示出与港口内站点的差异，包括物理化学变量，即：一个）涨潮期间的技术支持服务、磷酸盐、硝酸盐；b) 酸碱度、做、TDS、浊度、退潮时的技术支持服务。

关键词：控制站、丹戎艾玛斯三宝垄港、东亚季风、海水和沉积物、污染指数、主成分分析。

1. Introduction

Commonly used as the main commodity carriers, commercial vessels are essential for the transportation system around the world. Thus, industrial activities and the population in the port area have been increasing. These conditions lead to pollution [11]. The port of Tanjung Emas (PTES) is on the north coast of Central Java Province, Indonesia. The port is located in an industrial, tourism, and trade area in Kelurahan Tanjung Mas whose maximum capacity of land and settlement has been exceeded. Moreover, there are also centrally distributed slums in the port and train station areas, which increase the burden on the environment [4].

PTES activities include the loading and unloading operations, and docking facilities. These docking activities potentially contribute to polluting the seawater. For example, painting particles on the vessel hull, cutting porous parts, etc. Ship repair waste, including paint residue, rust, and used oil, also potentially results in heavy metal Pb and Zn pollution in port waters [25]. This port also serves transportation between islands; loading and unloading of solid goods, unloading of wood logs, oil distribution, and LPG (Liquid Petroleum Gas) that could lead to contamination [12].

Moreover, the increase in vessel arrivals also resulted in pollution due to the ballast water discharged to the port waters. Ballast water is used to maintain vessel stability. The ballast tank is commonly filled up with seawater taken from the previous port waters and would be discharged at the destination port. Older ships potentially caused contamination of Pb in the port waters; 26.7% of them were old vessels. This condition caused the content of Pb in Dwitama dock to exceed the quality standards for port waters [2].

This research was aimed: a) to test the correlation of physical-chemical parameters at both high and low tide using Pearson correlation, b) to test the correlation of heavy metals (Pb, Cd, Cu, Zn) in seawater and sediment at both high and low tide, c) to perform cluster analysis on the stations at both high and low tide, d) to determine port waters Index of Pollution (IP), e) to identify factors that affect the port water pollution using PCA (Principal Component Analysis).

2. Materials and Methods

This study was descriptive research aimed to identify some facts of an object using a proper interpretation, random simple collection method, ratio scale of measurement scale, and secondary data [23]. The research variables included a) physical parameters (temperature, TSS, TDS, turbidity, brightness); b) chemical parameters (pH, salinity, BOD, phosphate, nitrate, sulfide, phenol); c) the content of heavy metals Pb, Cd, Cu, Zn in waters; d) the content of Pb, Cd, Cu, Zn in sediment. Research on sediment was also conducted to analyze the sediment texture in both the port basin and control station.

The research was conducted in July, August, and September 2016. At each of the 10 stations, the sampling was carried out thrice. Thus, there were 84 water samples to examine for both heavy metal content and physicochemical parameters. Alternatively, for the content of heavy metals in the sediment, the sampling was carried out twice in each station, so that 54 sediment samples were obtained. Samples for sediment texture were taken once so that there were 27 sediment samples.

2.1. Study Area

The research was conducted in PTES waters, Semarang City, Central Java province, Indonesia. Two control stations were employed in this research, i.e., control station at the estuary of the Banjir Kanal Timur (BKT) River and the estuary of the Siangker River. The research also randomly took samples from ten stations, latitude $6^{\circ}57.059' S - 6^{\circ}56.207'$ and longitude $110^{\circ}25.150' E - 110^{\circ}26.599' E$. The stations included a) Station 1, the estuary of the Kali Baru River; b) Station 2, Pusri Dock; c) Station 3, Sriboga Dock; d) Station 4, passenger dock of Pelni, Dharma Lautan Utama; e) Station 5, dock number 25 for solid and bulk cargo ship; f) Station 6, container ship dock; g) Station 7, the outflow from the port basin in the middle part of the port basin; h) Station 8, LPG dock; i) Station 9, the estuary of the Banjir kanal Timur (BKT), used as the control station, positioned at the eastern outer part of the port basin; and j) Station 10, the estuary of the Siangker River in the western part of the port basin, also as the control station (Figure 1).

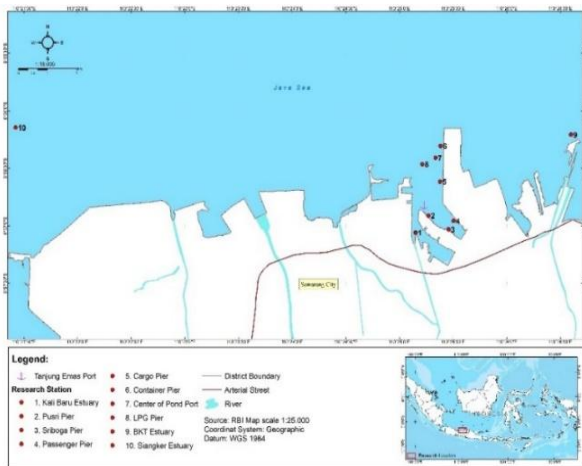


Fig. 1 Research sampling station

The samples were obtained using a Van grab. The samples were put into a new plastic bottle with diluted acidic water and taken to Regional Health Laboratory, Semarang. The samples were dried at 25°C for 24 hours, and filtered using a 100-micron sieve for the sample extraction preparation. AAS (Atomic Absorption Spectroscopy) was then carried out using argon gas furnaces and Pb, Cd, Cu, and Zn lamps [3, 11]. The other samples were also examined at the Marine Laboratory of Diponegoro University, Semarang, to analyze their sediment texture.

2.2. Sample of Seawater

The seawater samples were collected using Nansen bottles (three water samples were taken from one station: surface, middle, and bottom water) and put into 1 liter plastic bottle which had been sterilized using diluted acidic water. After 3 ml nitric acid was added, the samples were taken to Regional Health Laboratory, Semarang. The samples were homogenized using a stirrer, then put into 100 mL plastic bottles. The samples were analyzed using AAS [3, 11].

2.3. Statistical Analysis

Pearson correlation was applied to measure the correlation between the two variables linearly and the data were on a ratio scale. Pearson correlation degrees include a) very weak (0.00 – 0.199), b) weak (0.2 – 0.399), c) moderate (0.4 – 0.599), d) strong (0.6 – 0.799), and e) very strong (0.8 – 1.00) [21]. IBM SPSS version 25 was applied to perform the analysis. Factor analysis was aimed to define and analyze interconnected data by defining the structure dimensions and determining how far each variable could be described by each dimension. This research applied PCA (Principal Component Analysis) approach, which used an ordinary correlation matrix, correlation with itself. This PCA testing used the Barlett test of sphericity; if the result is significant, it means that the variables are correlated. The next test used MSA (Measure of Sampling Adequacy); if the value of MSA < 0.5, factor analysis cannot be carried out [10].

In this research, cluster analysis was also

implemented where objects were grouped based on characteristics; the same objects would be put into the same cluster. Cluster analysis answered the process through similarity measurement, cluster formation, and the number of clusters formed [29].

2.4. Data Analysis

2.4.1. Geoaccumulation Index and Pollution Load Index

The geoaccumulation index (I_{geo}) was used to calculate the pollution in sediments. I_{geo} for heavy metals was calculated using the following formula [13]:

$$I_{geo} = \frac{\log_2(C_n)}{1.5(B_n)}, \quad (1)$$

where C_n is the metal content obtained in the sediment and B_n is the natural chemical content in metal (n). I_{geo} value range included a) ≤ 0 (unpolluted), b) 0-1 (unpolluted to moderately polluted), c) 1-2 (moderately polluted), d) 2-3 (moderately polluted to severely polluted), e) 3-4 (severely polluted), f) 4-5 (severely polluted to extremely polluted), g) > 5 (extremely polluted). The basic metal values used in this research were 20 mg/kg for Pb, 0.3 mg/kg for Cd, 95 mg/kg for Zn, and 35 mg/kg for Cu [28]. Factor 1.5 was the basic matrix of correction factors. PLI (Pollution Load Index) is used to calculate the pollution level caused by heavy metals in sediment, using the following formula [13, 1]:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n} \quad (2)$$

where CF obtained by

$$CF = \frac{C_{metal}}{C_{baseline}} \quad (3)$$

The pollution index in waters was examined to analyze the pollution level [17, 7]:

$$PI_j = \sqrt{\frac{(C_i)_{Max}^2 + (C_i)_{Av}^2}{L_{ij}^2}} \quad (4)$$

where PI_j (pollution index to j), C_i (water quality concentration to i), L_{ij} (water quality standard on j), Max (Maximum), Av (average).

3. Results

Station 9 (BKT) is a control station located outside the port basin which was not affected by the basin waters. The average water temperature reached 30.88°C and ranged from 27.47 to 32.12°C, meeting the quality standards. The lowest water temperature was found at Station 9. It was also found that the water pH of the water ranged from 6.85 to 7.71, with the average reaching 7.42, which met the quality standards. The DO content ranged from 6.47 to 7.69 mg/l, with the average value reaching 7.31 mg/l. The lowest DO content was also found at Station 9. The average TDS value reached 733.97 mg/l, at a value of 502-656.17 mg/l. The highest value was found at Station 3. The average value of turbidity was 147.99 NTU, ranging from 27.54 to 716.99 NTU, exceeding the quality standard. The highest and lowest values were found,

respectively, at Station 4 and Station 9.

The brightness values of all stations had exceeded the quality standard, with the average value reaching 0.94 m, ranging from 0.3 to 1.23 m. The highest value was found at Station 4 while the lowest was found at Station 9. The average value of salinity reached 28.86 ppt, ranging from 27.2 to 29.58 ppt. The lowest value was found at Station 9 while the highest was found at Station 5. The average TSS value reached 109.59 mg/l, ranging from 23.67 to 302.17 mg/l. The TSS value at the control station 9 reached 121.33 mg/l, which was different from the waters in the port basin. The highest value was found at Station 7 and the lowest was at Station 6.

This TSS content had exceeded the quality standard. The BOD₅ values ranged from 0.35 to 0.44 mg/l, with the average value reaching 0.4 mg/l, which still met the quality standards. The value of BOD₅ at Station 4 was

the same as in the control Station 9. The average value of phosphate reached 0.69 mg/l, ranging from 0.58 to 1.17 mg/l. The lowest value was found at Station 1 while the highest was at Station 8. The value found at the control station was above the quality standard. The phosphate value was found above the quality standard. The average nitrate content reached 0.27 mg/l, ranging between 0.23 and 0.56 mg/l. The highest value was found at Station 9. The content of sulfide was out of the quality standard, with an average value of 0.03, the lowest value of 0.02 and the highest value of 0.04 (Station 1). The average value of phenol reached 0.03 mg/l, ranging from 0.03 to 0.04 mg/l, exceeding the quality standards. 7 out of 13 physico-chemical variables met the quality standards (temperature, pH, DO, TDS, salinity and BOD); while other 6 variables did not meet the quality standards (turbidity, brightness, TSS, phosphate, nitrate, sulfide and phenol) (Table 1).

Table 1 Physico-chemical parameters at high tides

Parameters	Sampling Field									Quality Standards [8, 22]
	1	2	3	4	5	6	7	8	9	
Temperature (°C)	31.78	31.6	31.05	31.25	31.18	30.43	32.12	31.03	27.47	28-32
Ph	7.09	7.52	7.67	7.58	7.59	7.37	7.38	7.71	6.85	7-8.5
DO (mg/l)	7.26	7.25	7.6	7.19	7.54	7.46	7.33	7.69	6.47	> 5
TDS (mg/l)	644	626.83	656.17	632.67	620.5	502	583	560.83	513.67	2000
Turbidity (NTU)	54.76	131.89	75.72	716.99	85.76	28.23	144.69	66.32	27.54	< 5
Brightness (m)	0.89	1.04	0.99	1.23	1.19	0.99	0.93	0.88	0.3	> 3-5
Salinity (ppt)	29.08	29.32	29.42	29.38	29.58	28.1	29.07	28.63	27.2	33-34
TSS (mg/l)	77.67	118.67	95.17	56.17	31.67	23.67	302.17	159.83	121.33	20-80
BOD (mg/l)	0.39	0.4	0.44	0.43	0.35	0.36	0.42	0.42	0.43	20
Phosphate (mg/l)	0.58	0.61	0.8	0.66	0.72	0.64	0.73	1.17	1.01	0.015
Nitrate (mg/l)	0.23	0.23	0.26	0.23	0.23	0.23	0.23	0.23	0.56	0.008
Sulfide (mg/l)	0.04	0.03	0.03	0.03	0.02	0.02	0.03	0.03	0.02	0.01
Phenol (mg/l)	0.04	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.03	0.02

The temperature at low tide, at night, was lower than the temperature at high tide, with an average value reaching 28.89°C, ranging from 27.13°C to 29.42°C. At BKT, the temperature reached 28.3°C, which was lower than the stations in the port basin. The average pH value reached 7.24, ranging from 6.64 to 7.64. The

lowest pH was found at the control station while the highest was at Station 5. The average value of DO content reached 6.79 mg/l, ranging from 4.75 to 12.04 mg/l. The lowest was found at the control station, while the highest was at Station 5 (Table 2).

Table 2 Physico-chemical parameters at low tides

Parameters	Sampling Field									Quality Standards [8, 22]
	Sta 1	Sta 2	Sta 3	Sta 4	Sta 5	Sta 6	Sta 7	Sta 8	Sta 9	
Temperature (°C)	27.13	29.42	29.22	29.07	29.2	29.22	29.1	29.32	28.3	28-32
Ph	7.38	7.34	7.64	7.57	7.26	7.01	7.11	7.21	6.64	7-8.5
DO (mg/l)	6.08	6.21	5.77	6.09	12.04	6.7	6.79	6.66	4.75	> 5
TDS (mg/l)	464.83	470.5	456.67	438.5	471	423.17	458	473	425.33	2000
Turbidity (NTU)	33.25	45.76	53.76	18.71	39.49	74.67	66.2	34.99	26.17	< 5
Salinity (ppt)	25.9	28.53	28.63	28.78	28.85	29	29.32	28.95	23.18	33-34
TSS (mg/l)	11.17	33.83	26.33	9.33	44.83	28	222.83	151.67	12.17	20-80
BOD ₅ (mg/l)	0.37	0.35	0.36	0.32	0.37	0.32	0.5	0.45	0.33	5
Phosphate (mg/l)	0.17	1.01	1.64	0.39	0.63	1.34	1.6	1.87	0.49	0.015
Nitrate (mg/l)	0.43	0.23	0.39	0.23	0.23	0.27	0.23	0.32	0.53	0.008
Sulfide (mg/l)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.01
Phenol (mg/l)	0.03	0.04	0.03	0.03	0.03	0.03	0.02	0.02	0.03	0.002

The average value of TDS reached 608.1 mg/l, and the range of 423.17-473 mg/l. The highest value was found at Station 8 while the lowest was at Station 6.

The value of TDS at the control station 9 was low. The TDS value still met the quality standards. The turbidity values at all stations had exceeded the quality standards,

with the average value reaching 43.68 NTU, ranging from 18.71 to 74.67 NTU. The lowest turbidity was at Station 4, while the highest was at Station 6. However, the turbidity at the control station reached 26.17 NTU. The salinity level reached 23.28 and 29.32 ppt, with the lowest value found at the control station 9, the highest at Station 7. The average value reached 27.90 ppt, still meeting the quality standard. The average value of TSS (60.02 mg/l) still met the quality standards. However, the values at Station 7 and 8 exceeded the quality standards. At the BKT control station, the value was lower (12.17 mg/l) and still met the quality standards. The average values of TSS still met the quality standards.

The BOD₅ value had exceeded the quality standard value, which was below 5 mg/l, reaching 0.37 mg/l, ranging from 0.32 to 0.5 mg/l, and the highest value was found at Station 7. The phosphate content had exceeded the quality standards, whose average value reached 1.02 mg/l, ranging from 0.17 mg/l (lowest) to 1.87 mg/l (highest). The content at the control station was slightly lower than that found at the station in the port basin (0.49 mg/l). The average nitrate content was 1.02 mg/l, exceeding the quality standards, with the lowest at Station 2 (0.23 mg/l), and the highest at Station 9 (0.53 mg/l). The sulfide content had also exceeded the quality standard (at the average value of 0.02 mg/l), with the lowest value reaching 0.02 mg/l and the highest reaching 0.03 mg/l. The average value of phenol reached 0.03, exceeding the quality standards. The lowest value was found at Station 8 and the highest was at Station 2. The value at the control station was the same as those at Stations 1, 3, 4 and 6. On the physical-chemical parameters at low tide, there were only 12 variables, excluding brightness as it was at night. Six out of twelve physical-chemical variables met the quality standards (temperature, pH, DO, TDS, salinity, and BOD₅); while other 6 variables did not meet the quality standards (turbidity, BOD₅, phosphate, nitrate, sulfide and phenol).

There was a strong significant correlation between

these variables: temperature-DO (0.729, $p < 0.05$), brightness-pH (0.774, $p < 0.05$), and brightness-DO (0.723, $p < 0.05$). Moreover, DO-pH (0.836, $p < 0.01$) and brightness-temperature (0.804, $p < 0.01$) had a very strong correlation. There was a very strong correlation between salinity and other physical variables: salinity-temperature (0.857, $p < 0.01$), salinity-TDS (0.878, $p < 0.01$), and salinity-brightness (0.860, $p < 0.01$). However, there was a negatively strong significant correlation between nitrate-brightness (0.893, $p < 0.01$) and nitrate-salinity (0.788, $p < 0.05$) (Table 3).

There was a very strong positive relationship between BOD₅-TDS (0.709, $p < 0.05$) and BOD₅-TSS (0.891, $p < 0.01$), a strong positive relationship between phosphate-TSS (0.682, $p < 0.05$), sulfate-TDS (0.663, $p < 0.05$) and sulfate BOD₅ (0.689, $p < 0.05$). There was a very strong negative significant relationship between nitrate-salinity (0.768, $p < 0.01$), phenol-TSS (0.767, $p < 0.01$), phenol-BOD₅ (0.835, $p < 0.01$); however, there was a strong relationship between phenol-sulphide (0.707, $p < 0.05$) (Table 4).

There was a strong significant positive correlation between Cu_{sed} and Cd_{sed} (0.764, $p < 0.05$); there was a strong significant positive correlation between Pb_{sed} with metals in sediment, including Pb_{sed}-Cd_{sed} (0.831, $p < 0.001$) and Pb_{sed}-Cu_{sed} (0.932, $p < 0.01$). There was a strong positive correlation between Zn in sediment and other metals in sediment, including Zn_{sed}-Cd_{sed} (0.689, $p < 0.05$); there was a very strong positive correlation between Zn_{sed}-Cu_{sed} (0.963, $p < 0.01$) and Zn_{sed}-Pb_{sed} (0.872, $p < 0.01$) (Table 5).

During low tide, there was a strong significant positive correlation between Cu_{sed}-Cd_{sed} (0.764, $p < 0.05$). For Pb metals in sediment, there was a very strong relationship between Pb_{sed}-Cd_{sed} (0.831, $p < 0.01$) and Pb_{sed}-Cu_{sed} (0.932, $p < 0.01$). There was a strong correlation between Zn_{sed}-Cd_{sed} (0.689, $p < 0.05$); there was a very strong correlation between Zn_{sed}-Cu_{sed} (0.963, $p < 0.01$) and Zn_{sed}-Cu_{sed} (0.872, $p < 0.01$) (Table 6).

Table 3 Pearson correlation between physicochemical variables at high tides

	Temp	pH	DO	TDS	Turb	Bright	Salinity	TSS	BOD ₅	P	N	S	P
Temp	1												
pH	0.606	1											
DO	0.729*	0.836**	1										
TDS	0.641	0.419	0.343	1									
Turb	0.225	0.287	-0.074	0.347	1								
Bright	0.804**	0.774*	0.723*	0.579	0.479	1							
Salinity	0.857**	0.696*	0.641	0.878**	0.366	0.860**	1						
TSS	0.191	-0.049	-0.059	-0.082	-0.120	-0.272	-0.038	1					
BOD ₅	-0.178	-0.006	-0.285	0.154	0.317	-0.345	-0.102	0.492	1				
P	-0.502	0.034	-0.071	-0.430	-0.255	-0.548	-0.483	0.301	0.432	1			
N	-0.937	-0.723	-0.856	-0.492	-0.222	-0.893**	-0.788*	0.047	0.339	0.466	1		
S	0.611	0.076	0.214	0.642	0.184	0.202	0.467	0.266	0.344	-0.239	-0.429	1	
Phe	0.287	0.006	0.042	0.517	0.478	0.460	0.467	-0.482	-0.338	-0.438	-0.275	0.250	1

Notes: Temp (Temperature), Turb (Turbidity), P (Phosphate), Bright (Brightness), N (Nitrate), S (Sulfide), Phe (Phenol)

* Correlation is significant at the 0.05 level (2 tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 4 Pearson correlation matrix between physicochemical variables at low tide

	Temp	pH	DO	TDS	Turb	Salinity	TSS	BOD ₅	P	Nitrate	Sulfide	Phenol
Temp	1											
pH	-0.049	1										
DO	0.189	0.109	1									
TDS	-0.254	0.406	0.307	1								
Turb	0.234	-0.068	0.053	0.246	1							
Salinity	0.362	0.556	0.398	0.424	0.514	1						
TSS	0.088	-0.135	0.091	0.421	0.436	0.451	1					
BOD ₅	-0.145	-0.001	0.081	0.709*	0.483	0.396	0.891**	1				
P	0.264	0.055	-0.077	0.382	0.691*	0.599	0.682*	0.650*	1			
Nitrate	-0.518	-0.350	-0.507	-0.059	-0.148	-0.768**	-0.259	-0.019	-0.125	1		
Sulfide	-0.307	0.017	-0.046	0.663*	0.261	0.290	0.475	0.689*	0.602	0.198	1	
Phenol	0.241	0.123	-0.017	-0.382	-0.356	-0.272	-0.767**	-0.835**	-0.580	-0.140	-0.707*	1

Notes: Temp (Temperature), Turb (Turbidity), P (Phosphate)

* Correlation is significant at the 0.05 level (2 tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 5 Pearson correlation matrix between metals at high tides

	Cd _{sw}	Cu _{sw}	Pb _{sw}	Zn _{sw}	Cd _{sed}	Cu _{sed}	Pb _{sed}	Zn _{sed}
Cd _{sw}	1							
Cu _{sw}	-0.315	1						
Pb _{sw}	0.376	-0.501	1					
Zn _{sw}	0.181	0.316	0.375	1				
Cd _{sed}	0.083	-0.195	0.271	0.431	1			
Cu _{sed}	0.044	-0.326	0.519	0.569	0.764*	1		
Pb _{sed}	-0.039	-0.092	0.259	0.650	0.831**	0.932**	1	
Zn _{sed}	0.144	-0.280	0.540	0.608	0.689*	0.963**	0.872**	1

Table 6 Correlation between metal variables at low tides

	Cd _{sw}	Cu _{sw}	Pb _{sw}	Zn _{sw}	Cd _{sed}	Cu _{sed}	Pb _{sed}	Zn _{sed}
Cd _{sw}	1							
Cu _{sw}	0.152	1						
Pb _{sw}	0.611	0.638	1					
Zn _{sw}	-0.215	0.520	0.241	1				
Cd _{sed}	0.191	0.033	0.153	-0.262	1			
Cu _{sed}	0.040	0.133	0.053	-0.012	0.764*	1		
Pb _{sed}	0.190	-0.045	0.153	-0.163	0.831**	0.932**	1	
Zn _{sed}	0.201	0.294	0.216	0.037	0.689*	0.963**	0.872**	1

Based on the agglomeration schedule, there were four clusters. The first cluster consisted of Stations 7 and 8 (with Euclidean distance reaching 3.158), the second cluster included Stations 2-4 and Stations 5-6 (with distances reaching 3.251 and 3.815). The third cluster comprised Stations 2 and 3 with distances reaching 5.293, and the fourth cluster included Stations 1 and 9 with distances reaching 6.311. This condition occurred because, at low tide, the current outside the port moved from the east to the west, while the current inside the port basin moved from the estuary of the Kali Baru out of the port basin. The descending order of the pollution levels by station was 7>6>4>1 (Figure 2a).

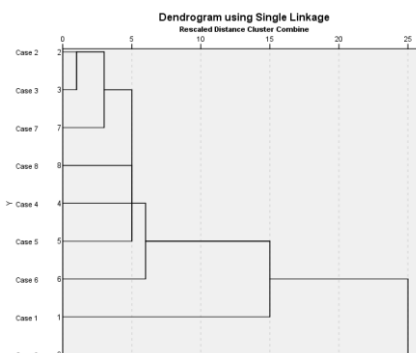
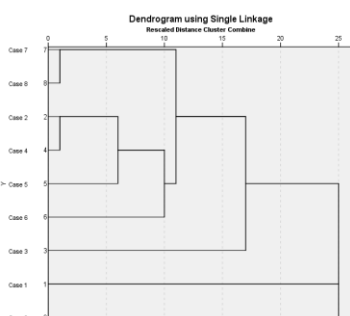


Fig. 2 Cluster analysis: a) At low tide (4 clusters), b) At high tide (3 clusters)

There were three clusters at high tides. The first with the closest Euclidian distance was Stations 2 and 3 (distance coefficient reaching 3.488). The second pair was Station 2 with Stations 7, 8, 4, 5 and 6 whose distance ranged from 3.488 to 3.941. The third pair was Stations 1 and 9, whose distance reached 8.035. Dominantly, during the high tide, the current moved from the west to the east, while in the port basin, the current moved toward the mouth of the Kali Baru. This

condition caused heavy metals with the highest value to be around the estuary of the Baru River. Thus, the descending order of the heavy metal pollution by the station was 1>3>7 (Figure 2b).

The content of Cd in seawater during the high tide ranged from 0.06 to 0.08 mg/l, with the maximum value found in the estuary of the Kali Baru. The content of Cu ranged between 0.05 and 0.13 mg/l, with the maximum value found in the BKT estuary. The content of Cd and Cu exceeded the port quality standards (0.01 mg/l). The content of Pb ranged from 0.41 to 0.49 mg/l, with the maximum value found in the bulk flour dock and the minimum value found in the estuary of the Siangker River and BKT. The content of Zn was 0.04 and 0.07 mg/l, with the maximum value found at the container ship dock. The content of Pb and Zn in seawater also exceeded the port quality standards. In a

descending order, the content of heavy metal in this research was Pb>Cd>Cu>Zn (Figure 3).

The content of heavy metal Cd in seawater ranged from 0.06 to 0.09 mg/liter, with an average value reaching 0.07 mg/l. The maximum content value of Cd was found in the bulk flour dock. This value was above the threshold of quality standards for ports and biota. Cu values ranged from 0.04 to 0.24 mg/l, with a minimum value found in the control station, the estuary of BKT, while the maximum value was found in the bulk flour dock. The Cu content exceeded the port quality standards. Pb value ranged from 0.37 to 0.63, with the maximum value found at Station 7 (the estuary of the port basin). This value was 10.8 times higher than the port quality standard threshold. Zn values ranged from 0.03 to 0.09 mg/l, with the maximum value found in the bulk flour dock.

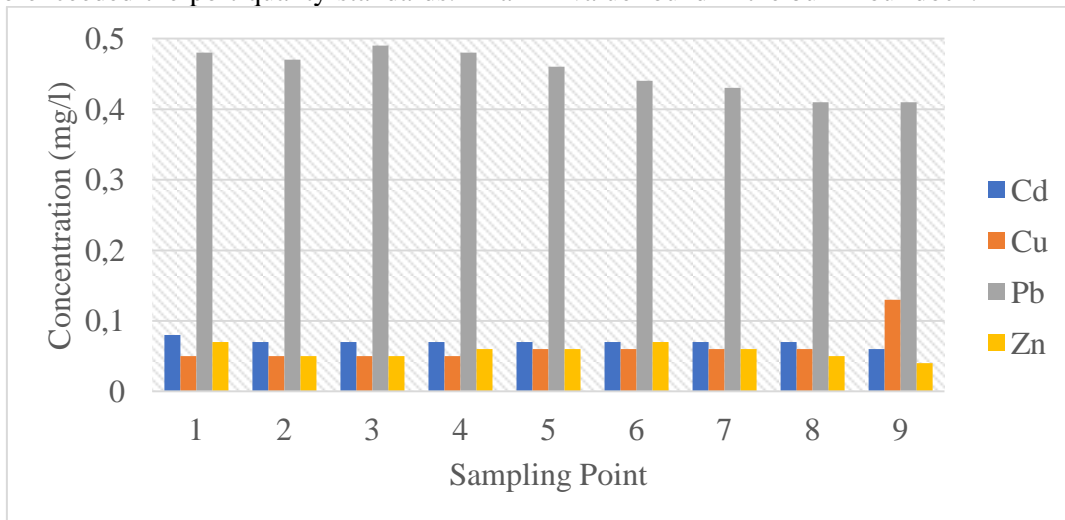


Fig. 3 Heavy metal concentrations in seawater at high tides

The content of Zn passed the quality standards for ports and biota. In a descending order, the content of heavy metals during low tide was Pb>Cd>Cu>Zn, greater than the content during high tide, because the

water volume decreased, leading to the increase in heavy metal concentration; the order of concentration both during high and low tide was the same (Figure 4).

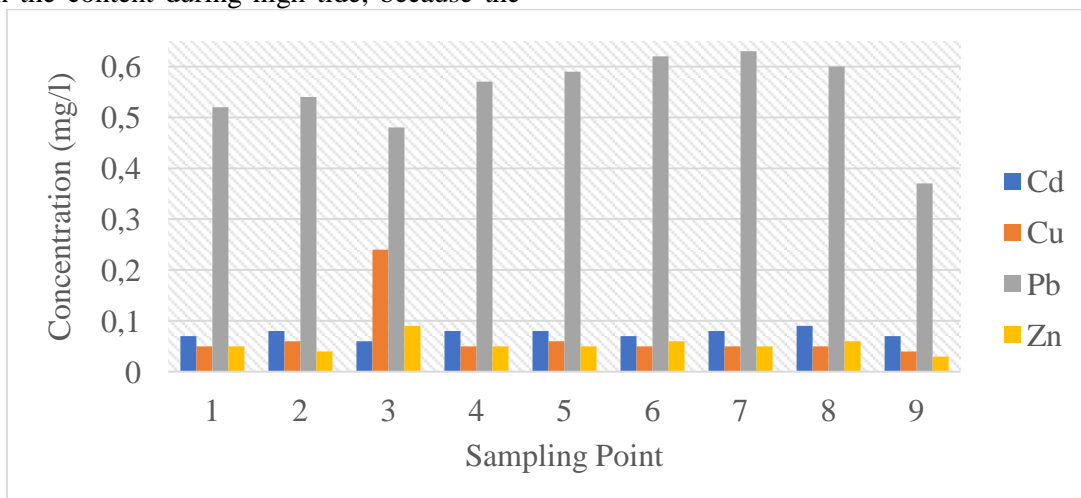


Fig. 4 The content of heavy metals in seawater at low tides

Zn content in the sediment ranged between 33.3 and 93.53 mg/kg, with an average value of 58.86 mg/kg. The maximum concentration of Zn was found in the

estuary of the Baru River, which is located in the port basin, while the lowest was found in the estuary of BKT. The estuaries of BKT (Station 9) and the

Siangker River were control stations located outside the port basin. The concentration of Pb in the sediment was at 9.33 and 30.87 mg/kg, with the maximum value found at Station 1, the estuary of the Kali Baru; while the lowest was found at the bulk flour dock. Alternatively, the control stations, the estuaries of BKT and the Siangker River were 10.14 and 18.47 mg/kg, respectively. The content of Cu reached 6.46 and 48.57 mg/kg, with a maximum value found in the estuary of the Baru River, and the minimum was at the estuary control station BKT. The content of Cd ranged from 0.32 to 0.47, with a minimum value found in bulk flour docks, and a maximum in the estuary of the Baru River. The maximum content of Zn, Pb, Cu, and Cd were found in the port basin, the estuary of the Kali Baru, which showed that the dominant current direction

moved toward the port basin and the river estuary in the port basin. In the descending order, the content of heavy metals in the sediment was Zn>Cu>Pb>Cd (Figure 5).

The accumulated index value (I_{geo}) in Zn ranged between 0.07 and 0.2, with an average value reaching 0.125, indicating that the sediment was nearly polluted by Zn. The control station (Station 9) showed a different value compared to the port basins. The value of I_{geo} on Pb reached 0.09 and 0.51, with a maximum value found at Station 7 and minimum at Station 3. The value of I_{geo} on Cu ranged between 0.04 and 0.3, with a minimum value at the estuary of BKT and a maximum at the estuary of the Kali Baru. These values indicated that Cu had polluted the sediment.

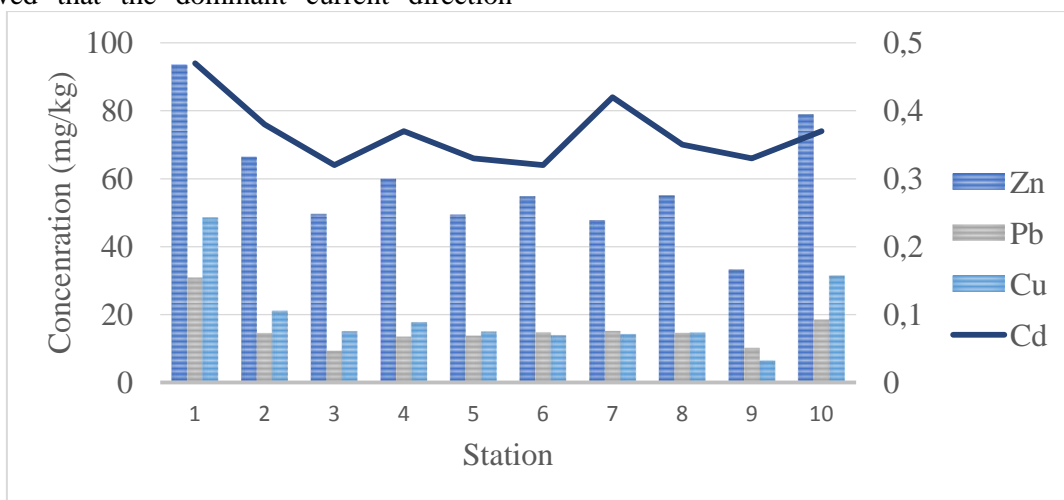


Fig. 5 The content of heavy metals in sediments during the East Asian Monsoon

Alternatively, the value of I_{geo} on Cd ranged between 0.21 and 0.31, with a minimum value found at Station 6, and a maximum on Station 1. The value of I_{geo} in metals Zn, Cu, and Cd was maximum in the estuary of the Kali Baru. The values of Cu, Zn, and Pb differed from the control stations, i.e., Station 2 (BKT

estuary) and Station 10 (Siangker estuary) compared to the stations in the port basin. In the descending order, the values of I_{geo} were Pb>Cd>Zn>Cu. The overall value of I_{geo} at all stations indicated that they were nearly moderately polluted (Figure 6).

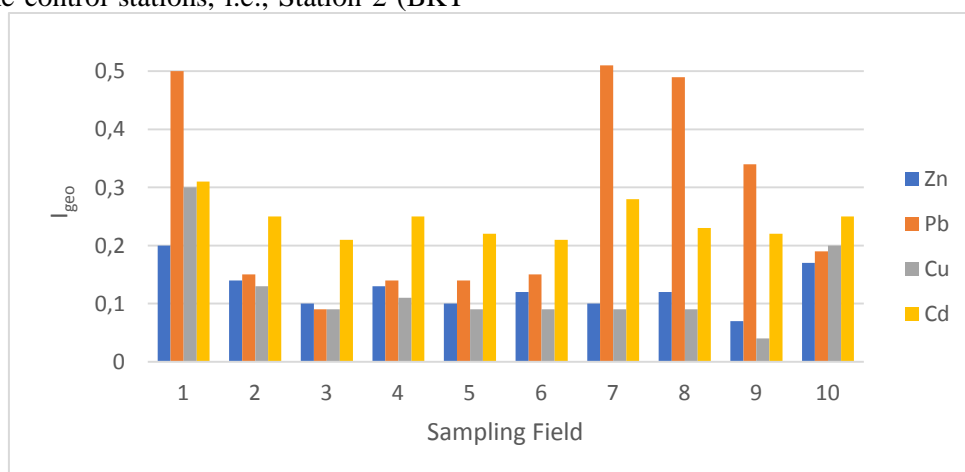


Fig. 6 The value of I_{geo} in sediments during the East Asian Monsoon

The PLI value for Zn metal ranged from 0.35-0.98, with the highest value found at the estuary of the Kali Baru. The PLI value for Pb metals was 0.78 on average, while the PLI for Cu metals ranged from 0.2-1.52. The

PLI values for Zn, Pb, and Cu metals indicated that there was no contamination. The value of PLI on Cd was 1.2 on average, with the highest value found in the estuary of the Kali Baru. The PLI condition on the Cd

metal indicated that pollution occurred. Overall, the estuary of the Kali Baru was the largest contributor to heavy metal contamination. In order, the PLI value of heavy metals in sediments was Cd>Pb>Zn=Cu (Figure 7).

Based on the value of PLI, it was found that the sediment pollution was caused by Cd and occurred in the estuary of the Kali Baru. The sediment composition in the PTES water was dominated by mud. In the estuary of the Kali Baru, the mud was dominant (56%), followed by sand and clay. The fertilizer dock was dominated by mud, reaching 90%, followed by clay and sand. At the bulk flour dock, mud predominated as

high as in the fertilizer dock, followed by clay and sand. At Station 4 (passenger ship dock), mud was also predominant, followed by sand and clay. At dock number 25 (Station 5), where cargo ships docked, the dominance of mud was higher (92%), while at Station 6, the container ship dock, the dominance of mud was the largest (94%), as was found at Stations 9 and 10. The predominance of mud was also found in Station 7 (output flow from the port basin), Station 8 LPG dock, Station 9 (BKT estuary) and Station 10 (the Siangker River estuary), so that at all stations, the sediment was predominated by mud (Figure 8).

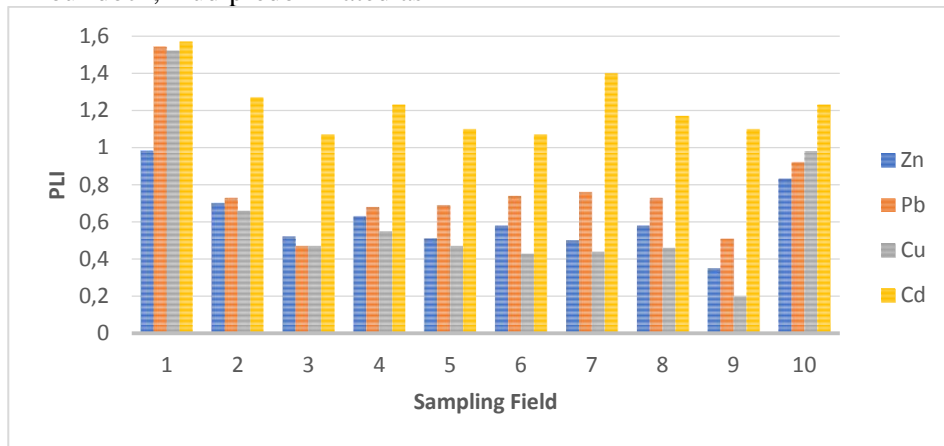


Fig. 7 PLI value in sediments

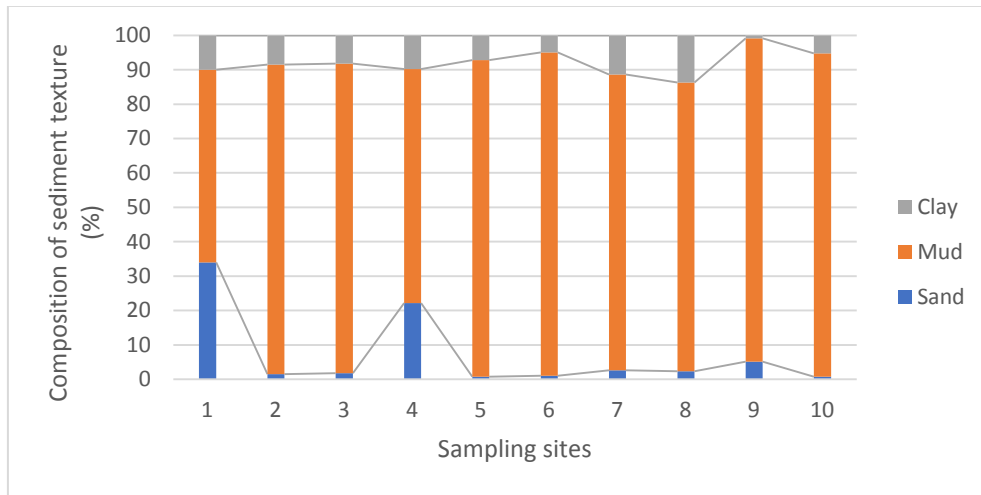


Fig. 8 Sediment texture in PTES water

The pollution index (IP) during low tide ranged from 12.28 to 655.76, with the maximum condition found at the bulk flour dock and the minimum at the passenger ship dock. At high tide, the IP ranged between 11.01 and 236.79, where the maximum IP was at the same station (bulk flour dock) while the minimum was found at the container ship dock. The IP value at low tide was greater than that at high tide. The IP at the bulk flour dock at low tide was 65.5 times greater than the maximum IP value, while at high tide, the IP was 23.7 times greater than the maximum IP. All stations at both low and high tides were classified as heavily polluted. At low tide, the control point (Station 9) had a different IP value compared to the conditions

in the port basin because at the estuary of BKT, the current moved to the west, so the levels of contamination decreased. However, in the port basin, the current moved from the estuary of the Kali Baru to the north, increasing the IP value as it moved to Station 2 (the fertilizer dock) and 3 (the flour dock) and decreasing as it moved to Station 4; the value increased again as it moved to the outside of the port. During high tide, the current moved into the port basin, so that the IP value at the LPG dock (Station 8) increased and continued to decline to Station 5, but increased on the fertilizer and flour dock and decreased at the estuary of the Kali Baru. This finding showed that at high and low tides, at the fertilizer and flour dock, the water was

trapped in the dock and could not circulate so the IP value reached the highest. The IP level at low tide was greater than that at high tide (Table 7).

Twenty-one variables were analyzed, including temperature, pH, DO, TDS, turbidity, brightness, salinity, TSS, BOD₅, phosphate, nitrate, sulfide, phenol, Cd in seawater, Cu in seawater, Pb in seawater, Zn in seawater, Cd in sediment, Cu in sediment, Pb in sediment, and Zn in sediment. Five factors (with eigenvalue >1) were considered, where factor 1 was

40.72%, factor 2 18.62%, factor 3 of 14.68%, factor 4 of 11.714%, and the remaining factor 5 6.5%. The number of these five factors 92.23% explained the factors, which affected pollution at high tides during the East Asian Monsoon in 2016, while the remaining 7.77% was influenced by other factors. All variables (21 variables) had a communality value of 1, which showed 92.23% of the total variance, with the largest communality value being found in turbidity (0.993) and the lowest being found in Zn in sediment (0.903).

Table 7 The Pollution index (IP) at high and low tides

No.	L _{ij}	Condition	Sampling Field								
			1	2	3	4	5	6	7	8	9
1	28	Low Tide	41.41	400.6	655.76	12.28	13.83	31.61	33.68	38.99	18.83
2	33	High Tide	17.34	227.43	236.79	60.25	15.15	11.01	18.82	17.76	24.26

Based on the matrix component and rotated matrix components as explained, there are 5 factors, which caused pollution at high tides: a) factor 1 including temperature (loading factor 0.949), pH (0.909), DO (0.922), brightness (0.863), salinity (0.838), and nitrate (-0.903); b) factor 2 including sulfide (0.785), Cu in seawater (Cu_{sw}) (-0.585), Zn_{sw} (0.588), Cu in sediment (Cu_{sed}) (0.918), Pb_{sed} (0.96) and Zn_{sed} (0.864); c) factor 3 including TSS (0.877), phenol (-0.528); factor 4 including turbidity (0.971), BOD₅ (0.791), phosphate (0.556), Cd_{sw} (0.97); and d) factor 5, including TDS (0.707) and Pb_{sw} (0.673) (Figure 9a).

At low tide, at night, 6 out of 20 variables (excluding brightness) which affected pollution during the East Asian Monsoon had eigenvalue > 1, with overall value reaching 92.88%, including factor 1 (28.93%), factor 2 (24.44%), factor 3 (16.84%), factor 4 (9.64%), factor 5 (7.83%), and factor 6 (5.2%). The remaining 7.12% were other factors that caused pollution at low tide. All variables showed initial commonalities 1, with the greatest value in nitrate (extraction factor 0.989), and the lowest in the DO (0.661). In the matrix component, the six factors, which affected (with the value of KMO [Kaiser-Meyer-Okkin] > 0.5) were a) factor 1 including salinity (loading factor 0.295), TSS (0.711), BOD (0.635), phosphate (0.728), nitrate (-0.775), Cu_{sw} (0.641) and Pb_{sw} (0.841); b) factor 2 including temperature (-0.743), Cd_{sed} (0.838), Cu_{sed} (0.945), Pb_{sed} (0.918) and Zn_{sed} (0.947); c) factor 3 including pH (0.599), phenol (0.726); d) factor 4 including DO (-0.509), Cd_{sw} (-0.538), Zn_{sw} (0.784); e) factor 5 including turbidity (0.694) and sulfide (-0.623); f) factor 6, including TDS (0.615) (Figure 9b).

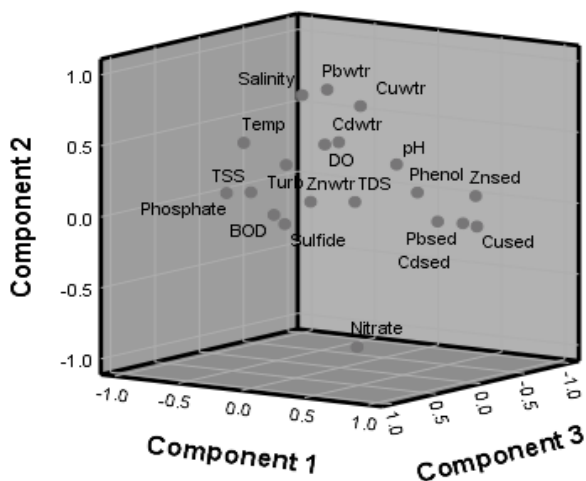
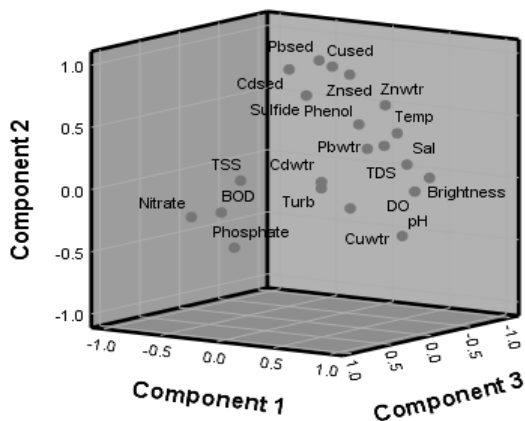


Fig. 9 Loading factors with PCA at: a) high tide, b) low tide

4. Discussion

The high content of Cu in PTES indicated that the area was close to the ship dock and the current during the low tide moved into the port waters [14]. The high content of Pb was caused by the waste of oil and coal; the value of Pb was higher than that of Cu because of the nature of Cu metal which quickly settled, compared to Pb [20]. This condition was in contrast to Suape Port in Brazil, where the accumulated value had not been polluted and affected by anthropogenic impacts [19]. The condition of sediment pollution agreed with research done in the Buriganga River (Dhaka, Bangladesh), which stated that Pb, Cd, and Cu metals caused PLI > 1 [1]. Research on sediments in Setiu Wetland, Malaysia identified the factors, which caused pollution, such as metal Pb and Cu, whose role in pollution reached 44.1%, while the cluster analysis of

Pb and Cu also gave a higher level in causing pollution [27].

The content of heavy metals in seawater at PTES exceeded the quality standards, excluding Zn; on the other hand, metals in sediments were still below the quality standards. The content of heavy metal Pb in seawater was the largest, while Zn was the smallest. The content of heavy metals in sediments was greater than in seawater. In descending order, the content level

of heavy metals in the sediment was Zn>Cu>Pb>Cd. However, research conducted in Balochistan, Pakistan showed that the Fe levels in seawater and sediments were the largest, while the smallest was Cd [5]. The content of heavy metals in Bastiong Port, Ternate, North Maluku, was smaller than in PTES; the content of Pb in the sediment was influenced by community waste disposal, such as battery plates and cans that contained Pb [18] (Table 8).

Table 8 The comparison of research on PTES and other research

Region	Pb	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Reference
	Seawater				Sediment				
PTES	0.5	0.08	0.07	0.06	15.51	0.37	19.84	58.86	This study
Ternate	-	-	-	-	4.59	-	3.86	-	[18]
Tulehu	0.05	0.002	-	-	5.41	0.89	-	-	[15]
Teluk Doreri	0.007	0.002	0.007	-	-	-	-	-	[24]
Gresik	-	-	-	-	3.37	2.96	0.08	5.87	[26]
Jeneberang	-	-	-	-	36	0.74	54.71	130.28	[28]
Yangtze River, China	0.83	0.04	1.47	8.91	25.8	0.13	19.7	71.5	[9]
(Quality standards)	0.05	0.01	0.05	0.1	-	-	-	-	[8]
(Quality standards)					30.2	0.7			[6]

The content of heavy metal Pb both at Tulehu Port, Central Maluku, and at PTES was on the threshold of quality standards. It was caused by waste discharged from fishing boats, fuel replacement, and mud sedimentation. The heavy metals Pb and Cd in sediments would provide a strong correlation to the decrease in the abundance and diversity of marine life [15, 16]. The content value of Cd metal in Doreri Bay, Manokwari, still met the quality standards for port waters, but the content had exceeded the quality standards for marine life (< 0.001 mg/l). This condition was caused by the activities in the port area, such as ship painting, ship docking, etc. affecting the bay waters [24].

The content value of heavy metals in the sediments in Gresik waters was smaller than that in the PTES, excluding Cd content in the sediments; in these waters, there were ports, industrial areas, and fish processing [26]. The content value of the heavy metals in the sediments in the Jeneberang River, Makassar, was higher compared to PTES's, which was influenced not only by volcanic weathering but also by household discharges of the dense settlements and disposal of residual boat fuel accumulated in the sediments [28].

The content value of heavy metals Pb, Cu, and Zn in seawater in the estuary of the Yangtze River was greater than in PTES waters, except for the Cu value; while in sediment, the contents of Pb and Zn were greater than in PTES sediment, excluding the content of Cu and Cd in sediment. These conditions showed that the pollution in the Yangtze River Estuary was mainly caused by run off, chemical liquid leakage, agricultural waste, and ship accidents [9].

5. Conclusion

At high tide, the control station (Station 9) has not

shown significant differences compared to the stations in the PTES basin, only on the parameters of temperature, brightness, and TSS. During this high tide, seven variables met the quality standards and 6 variables that did not. At low tide, the control station also showed differences in the parameters of temperature, pH, TDS, turbidity, and TSS. This condition was possibly caused by the control station located at the east of the adjacent PTES and was still affected by the PTES waters.

In terms of physico-chemical variables' correlation, there was a very strong positive correlation between the parameters of DO-pH, and temperature-brightness at high tide, while at low tide, there was a very strong correlation between BOD₅-TSS. Clustering carried out using cluster analysis at high tide found 3 clusters. Thus, in terms of pollution level, the descending order was 1>3>7; while at low tide, 4 clusters were found, 7>6>4>1.

In waters, the findings showed that Pb was found as the most dominant pollutant at both high and low tides (Pb>Cd>Cu>Zn). In sediment, Zn was the most dominant of all (Zn>Cu>Pb>Cd). The value of I_{geo} showed that the pollution in sediment was medium, and the order was the same as in the waters. However, based on the PLI value, the order was Cd>Pb>Zn=Cu with dominance on Cd. The value of IP at both high and low tide at all stations indicated that they were heavily polluted. Under these conditions, it was seen that the fertilizer and flour docks were heavily contaminated because the water at both docks was trapped and unable to circulate.

The pollution in the PTES waters was influenced by five factors, reaching 92.23%; while at low tide, there were six factors, reaching 92.88%. The natural and anthropogenic background factors such as salinity were the ones that influenced the heavy pollution in the

PTES.

The PTES is located between industrial areas, industrial docks in the port basin, slums, a ship waste holding facility, water treatment facility in both industrial and residential areas; this fact needs to be provided by the stakeholders. However, the supervisory function needs to be carried out by the government to supervise any activities both in the port and the surrounding area.

There is a difference in the accumulation of heavy metals at high tide or low tide, at low tide heavy metals accumulate on the outside toward the port, while at high tide it accumulates at the mouth of the Kali Baru. This is caused by differences in the flow of tidal or ebb currents. All research stations were classified as having heavy pollution. Both control stations (Siangker and BKT estuaries) showed differences with stations inside the port, including physico-chemical variables, namely:

- TSS, phosphate, nitrate during high tide conditions;
- pH, DO, TDS, turbidity, TSS at low tide.

This research is only limited to the East Asian Monsoon so to get the full condition of PTES, it is necessary to conduct research in the West Asian Monsoon and integrate it. The PTES port manager who obtained the Green Port Award should control water pollution, domestic waste and toxic waste from commercial vessels in collaboration with the port authorities through vessel inspections by the Marine Inspector. The management also needs to coordinate with the provincial environment agency to deal with pollution in the Kali Baru estuary.

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